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COMMUNICATION

Stepwise activation of "non-innocent" Cp* substituents – a Cp* based cascade reaction†‡

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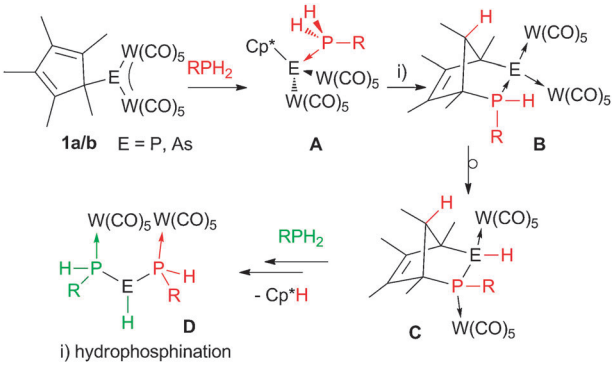
Reactions of Cp* substituted pentelidene complexes with the primary phosphine Cp^*PH_2 yield novel polycyclic phosphorus/arsenic and carbon containing cage compounds *via* cascade-like reactions. These reactions include a sequence of nucleophilic addition reactions, intramolecular hydrophosphination (partially hydroarsination) reactions, retro-Diels–Alder reactions with Cp*H elimination and subsequent [2 + 4]-cycloadditions.

Due to its special steric and electronic nature, the pentamethylcyclopentadienyl (Cp*) ligand is very often used in organometallic transition metal chemistry.[1] Moreover, it is also used in main group element chemistry since it shows a high flexibility in its coordination modes that can range from η^5 to η^1.[2] Only in some cases, the parent Cp ligand is unstable and undergoes transformation reactions (mostly [2 + 4]-cycloadditions) that are mostly induced by early transition metals.[3] For the Cp* ligand, only few examples are known like an uranium mediated coupling reaction[4] or Lewis acid induced Diels–Alder reactions on Cp* groups bound to P.[5] Furthermore, [2 + 3]-cycloaddition reactions[6] as well as the formation of cage systems are reported if Cp* is σ-bound at a main group element.[7]

We are especially interested in the reaction behaviour of special Cp* substituted phosphinidene and arsenidene compounds of the type $[Cp^*E\{W(CO)_5\}_2]$ (**1**: E = P (**a**), As (**b**)).[8] These compounds are versatile starting materials for the formation of transient complexes containing a pnictogen–tungsten triple bond,[9] for UV induced elimination reactions of a Cp* radical[10] and for migration reactions of the Cp* substituent that lead to pnictogen containing heterocycles.[11] Only if MesC≡P reacts with **1a**, a ring expansion of the Cp* substituent has been found so far.[12] In a recent study,[13] we observed that by using primary phosphines an addition to the Lewis acidic pentelidene atom occurs. So, a type **A** complex is formed that undergoes an intramolecular hydrophosphination reaction that leads to **B**. After rearrangement to **C**, a Cp*H elimination occurs. When adding a second equivalent of the phosphine, a stereoselective formation of triphosphines and 2-arsadiphosphines (**D**) coordinated by $W(CO)_5$ moieties was observed (Scheme 1) for which a diphosphene or arsadiphosphene intermediate was proposed.[14]



Scheme 1 Reaction sequence of the pentelidene complexes **1a**/**b** with primary phosphines.

The fact that the Cp* substituent can be eliminated as Cp*H by forming intermediates containing E=E multiple bonds raises the question if the reaction of **1** with Cp^*PH_2 facilitates the formation of P rich compounds. Indeed, we found out that by using this special primary phosphine the reaction does not stop at the stage of the triphosphines or arsadiphosphines. A sequence of subsequent reactions occurs to form unprecedented phosphorus/arsenic–carbon cage compounds by activation of the Cp* substituent, however. These results are reported herein.

The arsenidene complex $[Cp^*As\{W(CO)_5\}_2]$ (**1b**) ($Cp^* = C_5Me_5$) reacts with the primary phosphine Cp^*PH_2 in CH_2Cl_2 at room temperature to yield complex **2** that is stable as a crystalline solid in an inert atmosphere at 4 °C (*cf.* Scheme 2). The molecular structure of **2** (Fig. 1) shows a distorted heteronorbornene cage substituted by a phosphine ligand. All bond distances in the heteronorbornene unit in **2** can be described as single bonds with the exception of the double bond between C14 and C15. To some extent, related diphosphine compounds that contain the simple Cp moiety have been found by Niecke and Pietschnig[15] and Huttner and co-workers[16] *via* [2 + 4]-cycloaddition reactions of compounds containing P=P-double bonds with cyclopentadiene.

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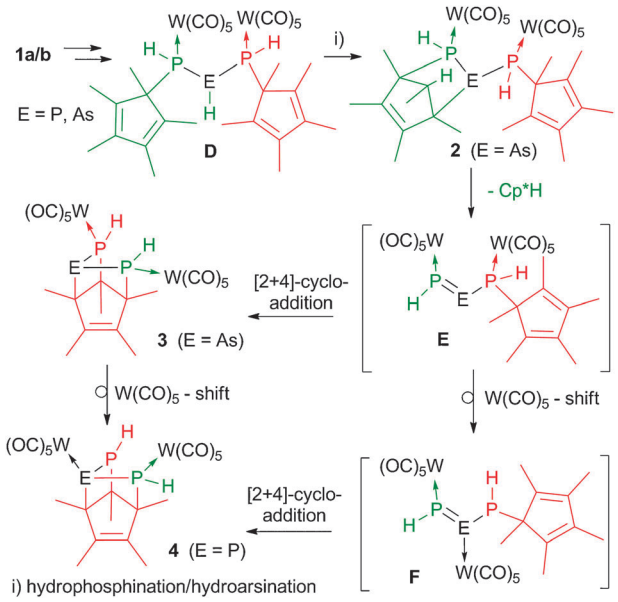
† Dedicated to Prof. Joachim Heinecke on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Experimental, theoretical and analytical details. CCDC 876640 and 876641. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc32690f



Scheme 2 Reaction sequence of the pentelidene complexes **1a**/**b** with Cp^*PH_2.

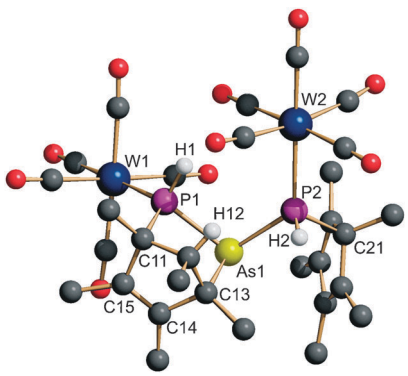


Fig. 1 Molecular structure of **2**. Hydrogen atoms of the methyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.5217(9), W(2)–P(2) 2.5491(10), As(1)–P(1) 2.3463(10), As1(2)–P(2) 2.3770(10), P(1)–C(11) 1.897(4), As1(2)–C(13) 2.060(4), P(2)–C(21) 1.903(3), C(14)–C(15) 1.345(5), P(1)–As1(1)–P(2) 102.14(3), C(11)–P(1)–As(1) 94.80(12), C(13)–As(1)–P(1) 85.93(10), C(13)–As1(1)–P(2) 101.18(10).

Besides the spectroscopic characterisation by multinuclear NMR and IR spectroscopy (*vide infra*), **2** was also characterized by mass spectrometry. The latter revealed the molecular ion peak and a peak corresponding to the loss of Cp*H.

An interesting reversible phenomenon was observed in the ^{1}H NMR spectrum of **2**. At 300 K, the spectrum shows only a set of signals of one conformer of **2**, while at 193 K two sets of signals corresponding to two conformers are monitored.[17] Obviously, the reason for the appearance of two conformers at low temperatures is the hindered rotation around the bond As1–P2 caused by the sterical demand of the tungsten pentacarbonyl and the Cp*-ligand at P2. Moreover, **2** eliminates Cp*H in solution after a few days at ambient temperature, which was detected by ^{1}H NMR. So, the novel arsadiphosphine cage complex **3** containing a Cp* ligand is formed. The ^{31}P NMR spectrum of **3** shows two pairs of doublets with $^2J_{P,P}$ coupling constants of 5 Hz and 11 Hz, respectively, that reveal the existence

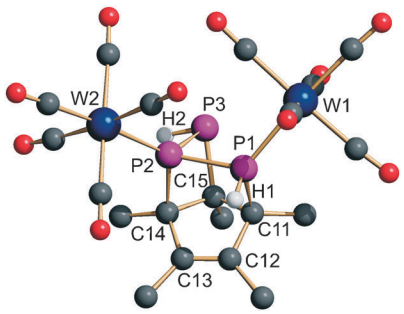


Fig. 2 Molecular structure of **4**, carbon-bonded hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.497(3), W(2)–P(2) 2.484(2), P(1)–P(2) 2.204(4), P(2)–P(3) 2.229(3), P(1)–C(11) 1.897(4), P(2)–C(14) 1.935(10), P(3)–C(15) 1.913(11), C(12)–C(13) 1.308(18), C(11)–P(1)–P(2) 89.1(3), P(1)–P(2)–P(3) 84.31(13), P(2)–P(3)–C(15) 73.9(3).

of two isomers of **3** in a ratio of 1 : 1. Each of the signals bears tungsten satellites. Furthermore, the molecular ion peak of **3** was detected by mass spectrometry.

Unlike the arsenidene complex **1b**, the phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ (**1a**) reacts with the primary phosphine Cp^*PH_2 in CH_2Cl_2 at room temperature to yield the compound [6,8]-dipentacarbonyltungsten(0)-[1,2,3,4,5]-pentamethyl-6,7,8-triphospha-tricyclo-[3,3,0,$0^{2,7}$]-3-octene (**4**) as the only isolable product. Product **4** represents a P containing congener of **3**. In solution, the structure of **4** remains intact and shows three doublets of doublets of doublets in the ^{31}P{H} NMR spectrum (δ = 6.9 (P1), 10.2 (P2), −65.3 (P3)) featuring a large coupling constant of 153 Hz between the not bound atoms P1 and P3 (*cf.* Fig. 2). A coupling through space is conceivable as the distance between P1 and P3 only measures 2.974(4) Å. Furthermore, the ^{31}P NMR spectrum of the isolated solid reveals a diastereomer of **4** that was detected in a ratio of 7 : 1 as the minor component. Repeated recrystallization strongly increases the percentage and purity of the major product **4** (with respect to its diastereomer). ^{1}H, ^{31}P{H}, ^{31}P, ^{13}C, HMBC, HSQC and ROESY NMR studies[17] of the reaction mixture confirmed that **4** is the main product and not its diastereomer.

The molecular structure of **4** (Fig. 2) can be regarded as a heteronorbornene cage with an additional bridge (P3) linking the atoms P2 and C15. All bond distances in the molecule can be described as single bonds with the exception of the double bond between C12 and C13. The W–P distances are comparable to those in $[W(CO)_5PH_3]$ (2.491(2) Å).[18] The all-carbon analogue of **4** was first characterized by Freeman and Rao *et al.* by NMR spectroscopy.[19] Phosphorus–carbon cage compounds synthesised by cycloaddition reactions were reported by Streubel, Lammertsma and Mathey *et al.*[20]

The results show that the introduction of a Cp* containing primary phosphine prolongs the reaction sequence shown in Scheme 1 from the pentelidene complexes **1a**/**1b** to the triphosphine/2-arsadiphosphine (**D**) *via* hydrophosphination reaction, isomerisation and retro [2+4]-cycloaddition with Cp* elimination by a cascade of subsequent reactions.

The formation of the novel cage compounds can be explained by a hydrophosphination/hydroarsination reaction of **D** that yields **2** followed by a retro [2+4]-cycloaddition. So, Cp*H is eliminated and the intermediate **E** is formed. At this stage of the reaction, two

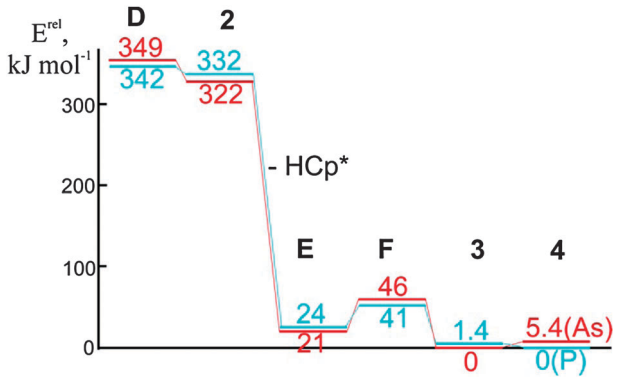


Fig. 3 Energetic profile for the reactions shown in Scheme 2. E = P (blue) and E = As (red). Only data for the most stable isomer are given.[17]

ways are possible for the phosphorus derivative. First, an intramolecular [2+4]-cycloaddition occurs to form the phosphorus analogue of **3**, which is followed by a tungsten pentacarbonyl shift. In the second way, the tungsten pentacarbonyl shift occurs first to form the intermediate **F**, which is followed by an intramolecular cycloaddition to yield **4**. In the case of the arsenidene complex **1b** that starts from the intermediate **E**, only the intramolecular [2+4]-cycloaddition was observed to give **3** due to the energetically unfavoured tungsten pentacarbonyl shifts from arsenic to phosphorus atoms. It is to mention that if the Cp^{Et} substituted (Cp^{Et} = η^5-C_5Me_4Et) pentelidene complex [$Cp^{Et}E\{W(CO)_5\}_2$] (**1c**) is used, the related compounds of **2**, **3** and **4** are obtained.

Moreover, the reaction pathway was investigated by DFT[17] calculations (Fig. 3). The transformation of **D** to **2** is exothermic (10 and 27 kJ mol^{-1} for E = P and As, respectively). The subsequent elimination of Cp*H is highly exothermic in both cases. In agreement with experimental observations, **3** is predicted to be most stable in the case of E = As, while **4** is most stable in the case of E = P. The intermediate **F** is about 17–25 kJ mol^{-1} higher in energy than **E**.

In summary, we explored the reaction pathway of the cascade reaction between the pentelidene complexes **1a**/**b** and Cp^*PH_2. They undergo a sequence of nucleophilic addition reactions, intramolecular hydrophosphination (or hydroarsination) reactions, retro-Diels–Alder reactions with Cp*H elimination and subsequent [2+4]-cycloaddition reactions. Tungsten pentacarbonyl migrations follow which yield novel polycyclic phosphorus/arsenic and carbon containing cage compounds. Due to the use of Cp* substituents at the pentelidene atom and at the primary phosphine, the sequence of hydrophosphination and subsequent Cp* elimination *via* a retro-Diels–Alder reaction takes place two times. The novel compounds represent triphosphines and arsadiphosphines unprecedentedly incorporated into carbon cage moieties that result from unusual activation of 'non-innocent' Cp* substituents.

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